Effect of Pd on Cu-Zn catalysts for the hydrogenation of CO_2 to methanol: stabilization of Cu metal against CO_2 oxidation

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A palladium–copper–zinc catalyst ($PdO:CuO:ZnO = 2:28:70$), prepared by sequential precipitation of the respective cations, was tested in the hydrogenation of CO_2 at high pressure (conditions: 60 bar, $CO_2:H_2 = 1:3$ (molar), $W/F = 0.0675\,kg\,h/m^3$, 453–513 K). The methanol yield was improved on using this Pd-containing catalyst at all temperatures with respect to the reference copper–zinc catalyst ($CuO:ZnO = 30:70$). This improvement was not due to an additional effect in which palladium was acting as an independent catalytic site but was caused by a synergetic effect of Pd on the active Cu sites. This effect was explained in terms of hydrogen spillover and an increased stability against CO_2 oxidation of the surface copper. Therefore, the present contribution not only supports previous literature findings concerning the hydrogen spillover mechanism but also resulted in a complementary view regarding the role of palladium in Pd-modified CuO-ZnO-based catalysts.

KEY WORDS: Pd-modified catalyst; copper–zinc catalysts; carbon dioxide hydrogenation; methanol synthesis; hydrogen spillover.

1. Introduction

Efficient heterogeneous catalysts have recently been developed for the hydrogenation of CO_2-rich mixtures to methanol, and pilot-scale plants based on this technology have been demonstrated [1]. Methanol is currently produced from synthesis gas ($CO/CO_2/H_2$) using a ternary Cu-Zn-Al oxide catalyst at 50–100 bar and 473–523 K [2]. Methanol synthesis from CO_2/H_2 feed is closely related to the fact that kinetic experiments, using isotope-labelled carbon oxides [3,4] and spectroscopic experiments [5], have demonstrated that under industrial conditions methanol is produced by hydrogenation of CO_2, with CO merely providing a source of CO_2 and acting as a reducing agent by scavenging surface oxygen. Nevertheless, the ternary catalyst that is active for CO-rich feed-stock is not so active for the CO_2-rich sources [6,7]. In addition, it has been reported that CO_2 keeps the copper surface partially oxidized during methanol synthesis [8,9]. The water formed as a byproduct, from both methanol synthesis and the RWGS side reaction, also has an inhibitory effect on the methanol synthesis because it also tends to oxidize the active copper metal during the reaction [10–12]. Within this context there have been many claims that the performance of the catalyst can be improved. The majority of the modified catalysts still contain Cu-Zn as the main components, together with different modifiers. Methanol synthesis from a CO_2/H_2 feed has already been improved by physically mixing a CuO-ZnO catalyst with a Pd catalyst [10–12] as well as by

using a Pd-impregnated CuO-ZnO-Al_2O_3 catalyst instead of physical mixtures [12,13]. The enhancement of the catalytic activity of these Pd-modified materials has been assigned to hydrogen spillover from metallic Pd to metallic Cu, the active component of the Cu-based catalyst.

Although it has been claimed that an H_2 spillover mechanism is responsible for the increase in the methanol yield for Pd-modified Cu-Zn(-Al) catalysts, other factors that can contribute should also be taken into account. The aim of the work described here is to present preliminary results regarding a mechanism for the promoting effect of Pd on the performance of the Pd-modified Cu-Zn catalyst in the hydrogenation of CO_2 to methanol. Besides the H_2 spillover mechanism, the influence of Pd on the redox properties of Cu metal was investigated.

2. Experimental

Two catalysts were prepared. A reference copper–zinc catalyst (CZ), with a nominal composition of $CuO:ZnO = 30:70$ (wt%), was prepared by coprecipitation of the corresponding metal nitrates at constant pH (*ca.* 7.0) and constant temperature (323 K) with sodium carbonate [14]. The precursor was prepared by simultaneously adding an aqueous solution of copper and zinc nitrates (total metal concentration $= 0.3\,M$) and an aqueous solution of sodium carbonate ($0.5\,M_0$) to a beaker containing a small amount of deionized water.

The suspension was vigorously stirred and kept at the desired pH by adjusting the relative flow rate of the two

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solutions. A palladium–copper–zinc (PCZ) catalyst, with a nominal composition of $PdO:CuO:ZnO = 2:28:70$ (wt%), was prepared by sequential precipitation in which palladium is first hydrolysed in the cation-containing vessel and then the $Pd(OH)_2$ suspension containing Cu^{2+} and Zn^{2+} cations is added to the reaction vessel to accomplish Cu-Zn coprecipitation through a hydroxycarbonate precursor.

The precipitates (precursors) were washed with deionized water to remove residual sodium (<0.1%), dried overnight and finally calcined at 623 K in air (catalyst). The catalyst powder was pelletized and sieved (0.4–0.5 mm) for subsequent characterization and use in kinetic experiments. The catalyst, diluted with SiC at a volume ratio of 3:1 to avoid thermal effects, was placed in a tubular reactor to carry out the catalytic activity test on CO_2 hydrogenation. The reaction was conducted at 60 bar overall pressure with a CO_2/H_2 mixture ($CO_2/H_2 = 1/3$) in a flow reactor at a W/F value of $0.0675 \, kg \, h/m^3$. The catalyst was reduced *in situ* at 513 K (heating rate 5 K/min) with a flow rate of 60 ml/min of a 10 vol% H_2/N_2 mixture for 2 h. The pretreating gases were flushed from the reactor with N_2 before the addition of the CO_2/H_2 mixture. When the system had reached the appropriate operating pressure the reaction temperature was increased gradually (2 K/min). Activity was measured at reaction temperatures between 453 and 513 K running from the lowest to the highest temperature and maintaining the reaction for 4 h at each temperature.

The effluents from the reactor were analysed on-line by gas chromatography using a Hewlett-Packard 5890 Series II gas chromatograph. The catalysts were characterized by powder X-ray diffraction on a computerized Seifert 3000 X-ray diffractometer using Cu K_α radiation, a PW 2200 goniometer (Bragg–Brentano $\theta/2\theta$), a bent graphite monochromator and an automatic slit. The copper surface area was measured using a nitrous oxide chemisorption method similar to that described by Chinchen et al. [15] and called reactive frontal chromatography (RFC). Once the catalyst was reduced in the H_2/N_2 mixture at 513 K for 2 h, it was exposed to a flow of N_2 and cooled to 333 K, the chemisorption temperature. A 3 vol% N_2O/N_2 gas flow was then fed into the reactor by switching a four-port valve. The delayed N_2O front produced by the decomposition of N_2O on the exposed Cu atoms could be monitored using a thermal conductivity detector.

The copper surface area was calculated assuming a molar stoichiometry of $N_2O/Cu_S = 0.5$ (where Cu_S denotes a surface copper atom) and value of 1.46×10^{19} Cu atoms/m^2 [16] for the copper surface-atom density, a value obtained on the assumption that the three most likely exposed planes for copper, *i.e.* (100), (110) and (111), are equally present at the surface. Temperature-programmed reduction experiments were carried out in a semi-automatic Micromeritics TPD/TPR 2900 apparatus.

The operating variables [initial amount of reducible oxides (S_0), total flow rate (V^*), heating rate (β) and the initial H_2 concentration (C_0)] were chosen in such a way that the H_2-consumption, line profile and peak position could be measured accurately [17,18]. For the sake of comparison, pure CuO and PdO (Aldrich) reference compounds were also measured. Reduction of Cu-containing samples started at 298 K, whereas values for those containing Pd were recorded after cooling the samples down to cryogenic temperatures (*ca.* 223 K). $H_2/CO_2/H_2$ redox cycles were performed in the same Micromeritics TPD/TPR 2900 apparatus. A redox cycle experiment consisted of five consecutive stages: (i) standard reduction of the catalyst from room (or cryogenic) temperature to 600 K and maintaining the sample at this temperature for 0.5 h (TPR_1), (ii) cleaning the catalyst surface with an He flow of 100 ml/min at 600 K for 0.5 h, (iii) introduction of CO_2 as an oxidizing agent (50 ml/min) at 600 K for 0.5 h, (iv) cleaning the surface once again with an He flow of 100 ml/min at 600 K for 0.5 h and cooling the sample down to room temperature and, finally, (v) a second standard TPR as described in step (i) (TPR_2).

3. Results and discussion

Methanol was produced by CO_2 hydrogenation and CO was simultaneously formed by the reverse water–gas shift (RWGS) side reaction. No other C-containing products were detected, except for some small traces of methane at high temperatures. The results derived from the catalytic tests are summarized in table 1.

The methanol yield (MTY), expressed as mole MeOH/(h kg cat), for the CZ catalyst is displayed as a function of reaction temperature in figure 1(A). The methanol yield was found to increase exponentially with increasing temperature without any decreasing or limiting value, indicating that there are no thermodynamic restrictions or diffusion limitations. The incorporation of Pd into the base CuO-ZnO components in the PCZ catalyst enhanced the CO_2 conversion to methanol for all temperatures studied (figure 1(A)). In

Table 1
Catalytic behaviour of the catalysts in the hydrogenation of CO_2

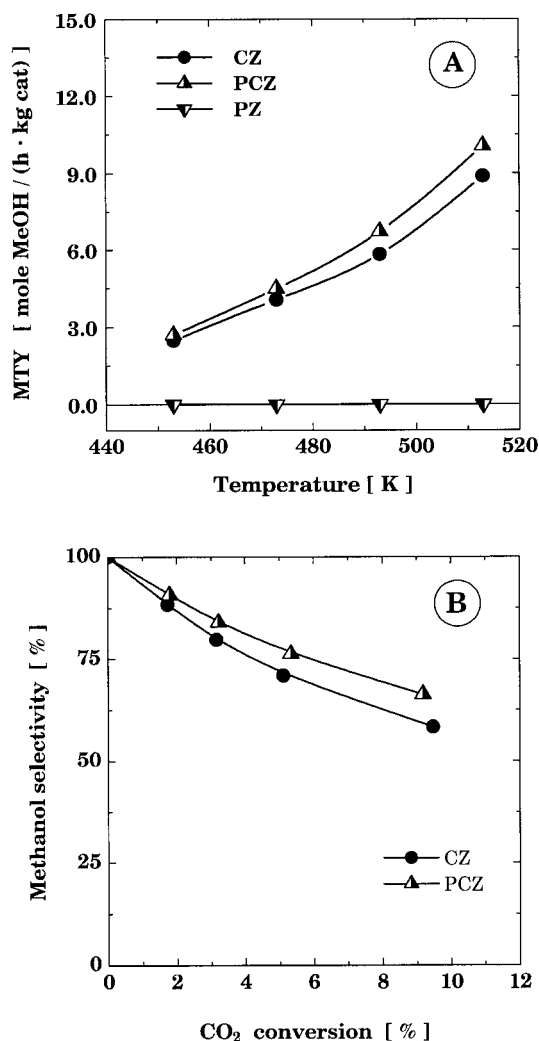|	Temperature (K)			
	453	473	493	513
CZ				
Conv. CO_2 (%)	1.74	3.16	5.11	9.48
Select. MeOH (%)	88.3	79.7	70.9	58.3
MTY [mole/(h kg cat)]	2.48	4.06	5.83	8.89
PCZ				
Conv. CO_2 (%)	1.80	3.23	5.34	9.19
Select. MeOH (%)	90.6	83.4	76.2	66.2
MTY [mole/(h kg cat)]	2.69	4.48	6.72	10.06

Figure 1. (A) Methanol yield [mole MeOH/(h kg cat)] as a function of the reaction temperature and (B) methanol selectivity against CO_2 conversion. Conditions: $P = 60$ bar, $CO_2/H_2 = 3$, $W/F = 0.0675$ kg h/m³ and $T = 453–513$ K.

order to rule out the possibility that the increase in MTY was only due to an additional effect caused by palladium, a reference catalyst PZ (2/98 wt% PdO/ZnO) was prepared by the sequential precipitation method. The absence of activity for this catalyst suggests that Pd did not act as an independent catalytic site for methanol synthesis but gave rise to a synergetic effect. As the selectivity towards MeOH, for the same CO_2 conversion, was higher for the PCZ than for CZ (figure 1(B)), it is clear that the enhancement in MTY is due to an increase in the selectivity but not in the CO_2 conversion. Therefore, the active centres are more selective for methanol synthesis. Such synergetic behaviour has already been reported for CuO-ZnO-based catalysts [10–13] and the enhancement was explained in terms of effective H_2 spillover generated by palladium.

Several techniques were applied in order to evaluate this synergetic effect in more detail. XRD analysis of the calcined catalysts (figure 2) only revealed the
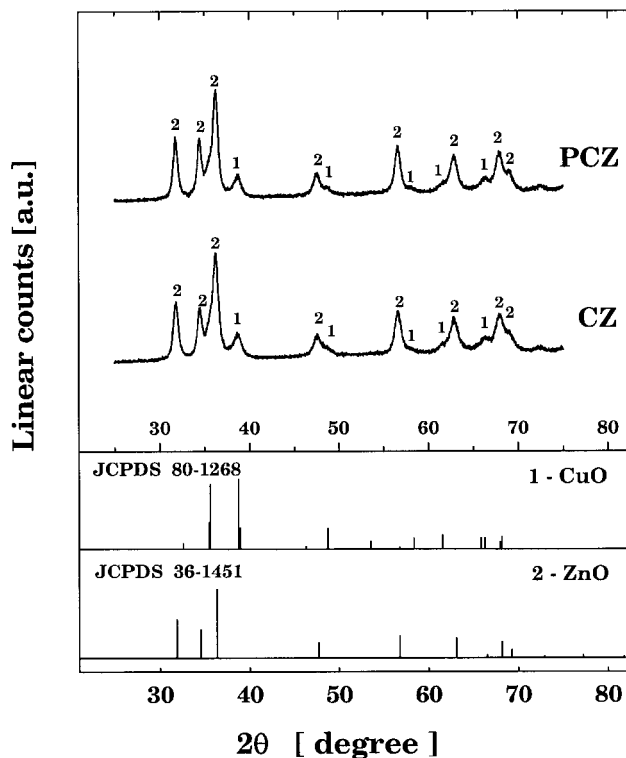

Figure 2. X-ray powder diffraction profiles of the calcined catalysts.

diffraction lines of CuO (JCPDS 80-1268 [19]) and ZnO (JCPDS 36-1451 [20]) crystalline phases. It can be seen that the peaks for CZ and PCZ are similar.

The line broadening of the CuO(111) diffraction line at $2\theta = 38.77°$ was used to calculate the mean crystallite size (D_{CuO}) using the Scherrer equation after Warren correction for instrumental line broadening ($D = K\lambda/\beta\cos\theta$ with $K = 0.9$). The CuO crystallite sizes for the calcined catalysts are given in table 2. The sizes were found to be very similar, with values around 9.5 nm. Similarly, the copper surface area determined by N_2O dissociative chemisorption on the H_2-reduced catalysts was almost the same for both samples (table 2). Therefore, it is clear that the enhancement in the methanol yield for PCZ cannot be explained by a modification of the copper dispersion associated with the incorporation of Pd.

Table 2
Summarized characterization data for the catalysts

Catalyst	XRD [D_{CuO} (nm)]	N_2O chemistry [exposed copper [a] (μmol CuS/g cat)]	TPR	
			[H_2/M]	Cu_{OX} (%) [b]
CZ	9.3	135.9 (5.7)	1.36	5.4
PCZ	9.6	126.9 (5.3)	1.64	2.0

[a] The values in parentheses represent square metres of copper per gram of catalyst (m² Cu/g cat), assuming 1.46×10^{19} Cu atoms/m².
[b] Amount of re-oxidized copper calculated as the ratio of H_2-consumption in TPR_2 and the H_2-consumption in TPR_1.
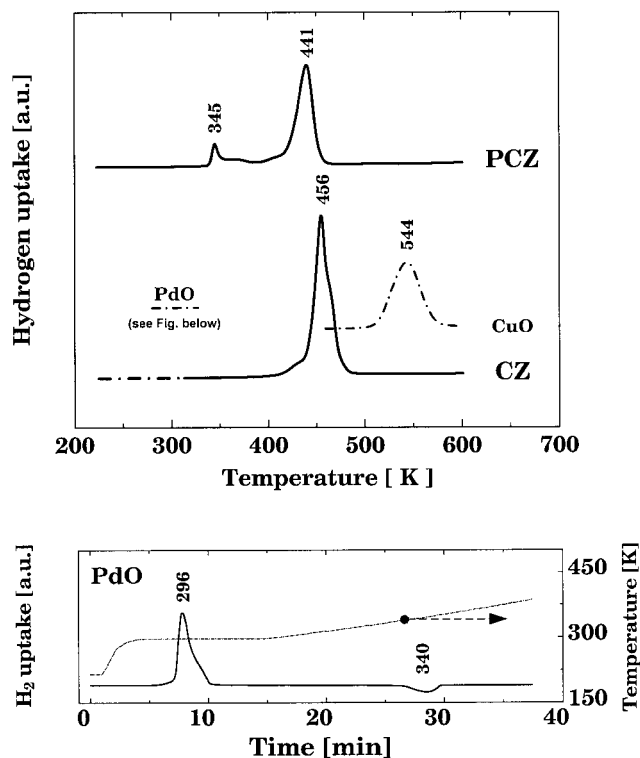
Figure 3. Temperature-programmed reduction profiles (TPR₁) for calcined samples with those of pure CuO and PdO as reference compounds.

TPR experiments gave very useful information concerning the influence of Pd on the CuO reducibility as well as direct information about the optimal activation pretreatment of the catalysts. The TPR experimental conditions were selected so that a good signal-to-noise ratio was obtained and the characteristic parameter P, as defined by the ratio $P = \beta(S_0/V^*)C_0$ [18] (the terms are defined in section 2) was about 2 K—a value in the range recommended in the literature to achieve good resolution of the reduction peaks. The TPR profiles (TPR₁) of the catalysts and those of pure CuO and PdO reference compounds are shown in figure 3. As PdO was reduced isothermally at room temperature (296 K) it was necessary to plot the hydrogen uptake against time (bottom curve in figure 3).

The TPR profile of the calcined CZ sample showed only one reduction peak, at around 456 K, which was assigned to the reduction of CuO to Cu: $CuO + H_2 \rightarrow Cu^0 + H_2O$. Although the reduction of zinc oxide is thermodynamically feasible at high temperatures, ZnO was not reduced under our experimental conditions. The presence of only one peak in the TPR profile of CuO is in accordance with the literature, although the temperature of the maximum H_2-consumption is different from the temperatures published previously [21–23]. The reduction peak of CuO for the CZ catalyst was displaced by almost 90 K towards lower temperatures in comparison with that of the CuO reference compound. This result indicates that the ZnO had enhanced the reducibility of the copper oxide phase and agrees with previous

observations [23]. In addition, the ratio between the amount of hydrogen consumed and the amount of reducible species present (H_2/M ratio in table 2) was determined quantitatively.

The difference between the theoretical and experimental values, i.e. $(H_2/M)_{exp} = 1.36$ and $(H_2/M)_{theor} = 1.00$, could be due to hydrogen sorbed on the catalyst. It is known that ZnO is capable of occluding large amounts of hydrogen [24,25] and it is this additional hydrogen, whether adsorbed on the surface or stored in the crystalline ZnO structure, that could be responsible for the increase in the $(H_2/M)_{exp}$ value for the CZ sample. On the other hand, the PCZ catalyst showed two peaks at 345 and 441 K. Comparing this profile with the one obtained for pure PdO, it can be seen that the reduction peak at 296 K, corresponding to isolated PdO phases, does not appear. This indicates that the PdO phase is well dispersed and interacting with the CuO-ZnO bulk oxides, making the reduction of PdO more difficult. In addition, the H_2 consumption at 345 K not only corresponded to palladium oxide reduction ($PdO + H_2 \rightarrow Pd + H_2O$) but also to partial Cu^{2+} (to Cu^0) reduction. This can be deduced by the fact that the H_2 consumption exceeded the stoichiometric amount of H_2 required for the complete reduction of PdO (nearly nine-fold higher).

The second peak at 441 K, which is shifted slightly but clearly towards lower temperatures with respect to the CZ catalyst, corresponds to the reduction of the remaining CuO to Cu metal. These features of CuO reduction, i.e. partial reduction of CuO at low temperatures and the shift of the main CuO reduction peak towards lower temperatures, point to a certain promoting effect of palladium. Moreover, the H_2/M ratio of the PCZ catalyst is higher than that of the corresponding CZ counterpart. The higher H_2/M ratio provides evidence for the existence of H_2 spillover. In conclusion, the enhancement of CuO reduction by Pd in TPR experiments suggests that the increase in the catalytic activity could be assigned to H_2 spillover from metallic Pd to metallic Cu, the active component of the Cu-based catalyst. The concentration of hydrogen available on the active centres is enhanced, a situation that improves the rate-determining step of the reaction mechanism (formate hydrogenation [26,27]). Moreover, the copper surface is maintained in a more reduced state, which counteracts the oxidizing effect of the CO_2 and/or H_2O byproduct.

It has been shown that $H_2/CO_2/H_2$ cycles constitute a very useful tool in determining the resistance of reduced Cu against oxidation [23]. These cycles were measured to determine the influence of Pd on the redox properties of the copper phase in the reduced catalysts. The fact that the oxidized Cu species, produced by treatment with CO_2 in the $H_2/CO_2/H_2$ cycles, can be related to similar oxidized species found under reaction conditions (CO_2/H_2) gives additional relevance to these kinds of experiments.
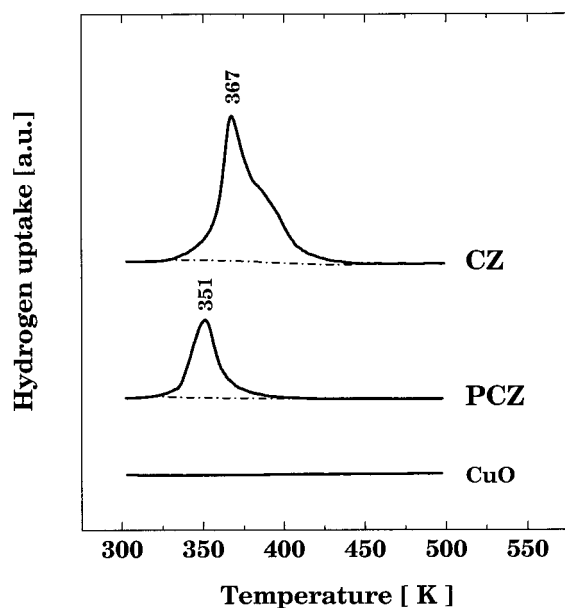
Figure 4. Temperature-programmed reduction (TPR$_2$) after CO_2 treatment at 600 K for 0.5 h. Pure CuO is also included.

The TPR profiles after CO_2 treatment at 600 K for the catalysts and pure CuO are shown in figure 4. It can be seen that the reduced CZ sample is partially oxidized by CO_2. The percentage of copper re-oxidized by CO_2 is determined as the ratio between the H$_2$-consumption in TPR$_2$ (figure 4) and the H$_2$-consumption in TPR$_1$ (figure 3). The amount of re-oxidized copper for the reduced CZ sample was 5.4%. This small amount, as well as the position of the peak maximum at low temperatures, suggests that surface Cu^+ species are generated during the CO_2 oxidation. It appears that the reduced pure CuO did not re-oxidize at all, as shown by the TPR$_2$ cycle. Both of these results have been described previously [22] and were explained in terms of a synergetic effect caused by the contact of CuO with ZnO particles in the binary system.

Two effects are found for the reduced PCZ catalyst when the H$_2$/CO$_2$/H$_2$ cycles are analysed. The first effect involves the shift to lower temperatures of the TPR$_2$ pattern for the PCZ catalyst in comparison with the CZ pattern. This enhancement in the reducibility of the surface copper species after CO_2 treatment (figure 4) agrees with the enhancement of bulk CuO reducibility in calcined PCZ catalyst—a phenomenon discussed previously (figure 3). In principle, both results indicate the H$_2$ spillover mechanism as being responsible for the promoting effect of Pd in Pd-modified Cu-Zn based catalysts.

Secondly, the amount of re-oxidized copper was significantly lower in comparison with the CZ catalyst, with values of 5.4% and 2.0%, respectively. This difference indicates that Pd stabilizes the copper particles against CO_2 oxidation and this fact could also explain the increase in the MTY for Pd-modified CuO-ZnO

catalysts, since it has been reported that CO_2 tends to oxidize the active copper metal during reaction [8,9]. The addition of Pd stabilizes the Cu particles against CO_2 oxidation during reaction and therefore counteracts this inhibitory effect. The same reasoning could be applied to the H$_2$O byproduct.

In conclusion, the modification of Cu surface redox properties of the PCZ catalyst suggests that a single phenomenon cannot explain the increase in the methanol yield. On the one hand, "more" separated Pd and Cu aggregates are present and these facilitate the H$_2$ spillover mechanism. On the other hand, there are more interacting Pd and Cu clusters present in which Pd, either by an "ensemble" or "ligand effect", modifies the surface redox properties of Cu. The formation of a Pd-Cu alloy at the PCZ catalyst surface could explain this phenomenon but more experimental work is required to confirm such hypothesis and provide a definitive interpretation. Both of these phenomena, H$_2$ spillover and the stabilization of Cu against CO_2 oxidation (hypothesis of Pd-Cu alloy formation), contribute to the enhancement of the methanol yield.

Acknowledgments

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